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Keywords	Epoxy resins; hyperbranched polymer;

	anionic homopolymerization; click reaction; azide-yne.
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Prof. Filip Du Prez
Universiteit Gent, Belgium

Tarragona, March 22th 2015

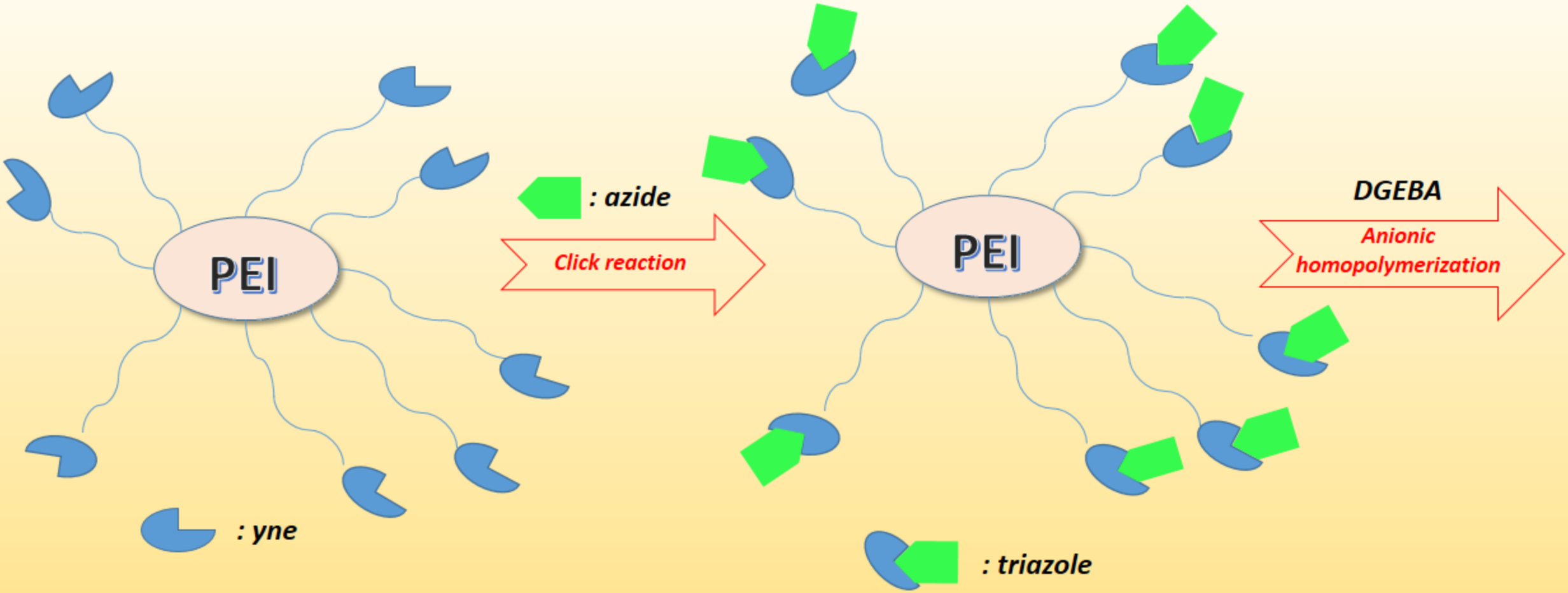
Dear Prof. Du Prez:

We send our manuscript entitled: "*Synthesis of 1,2,3-triazole functionalized hyperbranched poly(ethyleneimine) and its use as multifunctional anionic macroinitiator for diglycidyl ether of bisphenol A curing*" to be considered for publication in European Polymer Journal.

Looking forward to hearing from you, I remain.

Best regards,

Prof. Angels Serra


PEI
: azide
Click reaction
PEI
DGEBA
Anionic
homopolymerization
: yne
: triazole

By CuAAC click reaction hyperbranched poly(ethyleneimine) with terminal triazole has been prepared > This triazole functionalized polymer has been used as multifunctional macroinitiator for anionic epoxy curing > Triazole groups resulted less reactive than imidazole in anionic curing of epoxy resins> The use of this macroinitiator in epoxy curing leads to thermosets with submicron particles.

Synthesis of 1,2,3-triazole functionalized hyperbranched poly(ethyleneimine) and its use as multifunctional anionic macroinitiator for diglycidyl ether of bisphenol A curing

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Abstract

Hyperbranched poly(ethyleneimine) (PEI) has been modified by the addition of propargyl acrylate following a Michael addition reaction. On this polymer (PEI-yne) a copper (I)-catalyzed azide alkyne cycloaddition (CuAAC) has been performed to obtain a multifunctional triazole initiator (PEI-TA). After structural and thermal characterization this polymer has been used in different proportions as anionic multifunctional macroinitiator in diglycidyl ether of bisphenol A (DGEBA) homopolymerization. The curing process has been studied by calorimetry and the thermosets obtained have been thermally characterized and compared with thermosets prepared by using 1-methylimidazole (1-MI) as standard initiator. The electron microscopy inspection of the fracture surfaces of the new materials prepared shows the formation of submicrometer particles that should enhance toughness characteristics, changing smooth fracture surfaces in 1-MI initiated materials to multi-planar surface with tortuous and thicker cracks.

Keywords

Epoxy resins; hyperbranched polymer; anionic homopolymerization; click reaction; azide-yne.

1. Introduction

Epoxy resins are widely used in coatings, adhesives, molding compounds and polymer composites. These materials present good thermomechanical properties and excellent processability. The crosslinked epoxy polymers can be obtained by polycondensation reaction of epoxy monomers with amines, anhydrides or thiols, among others.[1]

Epoxy resins can also be crosslinked by ring-opening homopolymerization. This process requires the presence of an initiator. Among them, tertiary amines as imidazoles are extensively applied in anionic curing mechanisms.[2,3]

Recently, Ryu *et al.*[4] reported the synthesis of diglycidylether of bisphenol-1,2,3-triazoles (DGE-BPTs) and studied their self-catalyzed curing behavior. They found that DGE-BPT could be used alone to form a networked structure due to the catalytic effect of the triazole groups in the molecule. Non-isothermal differential scanning calorimetry analysis (DSC) showed large exotherms between 195 and 250ºC in all samples tested. Following a similar approach, nanocomposites of poly(triazole-ether-imidazole)s with epoxy-functionalized Fe_3O_4 nanoparticles were prepared with a strong interfacial interaction between inorganic particles and the polymer matrix. The presence of triazole and imidazole in the polymer structure led to crosslinked materials with enhanced thermal and mechanical properties.[5] The formation of thermosets by azide-yne reaction has been explored by Diaz et al.[6,7] They reported that high T_gs were obtained while the adhesion to copper substrates was highly enhanced. It was postulated that 1,2,3-triazoles have a good affinity to metallic surfaces and are far more stable than 1,2,4-triazoles to the attack by other chemicals.

Following these precedents, the aim of the present study was the synthesis of a multifunctional crosslinker with 1,2,3-triazole groups in its structure to prepare improved epoxy thermosets by anionic homopolymerization reaction. The multifunctionality of hyperbranched polymers (HBP) with a large amount of terminal groups will bring an advantageous approach to reach improved epoxy thermosets at convenient curing conditions. The use of hyperbranched polymers as multifunctional crosslinking agents has been previously explored by us.[8] An important improvement in mechanical and thermomechanical characteristics by adding these HBP modifiers to

epoxy thermosets are also foreseeable from our previous experience with 10-undecenoyl Boltorn modified HBPs or end-capped poly(ε-caprolactone) multiarm stars, among others.[9,10]

1,2,3-Triazoles were firstly prepared by Huisgen 1,3-dipolar cycloadditions.[11] Since then, several synthetic methodologies have been developed.[12,13,14] Click chemistry affords the [3 + 2] cycloaddition reaction between alkynes and azides leading to the formation of 1,2,3-triazoles moieties. Nowadays, the most used "click" reaction is the Cu^{I}-catalyzed azide/alkyne cycloaddition (CuAAC)[15,16] and a large variety of copper catalysts can be used as the catalyst. Usually, the reaction is performed with a Cu^{II} salt together with a reducing agent (usually sodium ascorbate) or a Cu^{I} compound. CuAAC reaction is fairly general with a broad range of alkynes and azides as starting materials. A wide variety of azides can be synthesized by SN_2 reactions from organic halides or arylsulfonates and sodium azide[17] and propargylic compounds can be easily prepared by different conventional methodologies.

To be used as a multifunctional crosslinking agent, in the present study, we have synthesized and characterized 1,2,3-triazole terminated poly(ethyleneimine) (PEI-TA), by the CuAAC reaction of an azide on propargyl functionalized poly(ethyleneimine) (PEI-yne), previously prepared by Michael addition reaction of commercially available poly(ethyleneimine) (PEI) on propargyl acrylate. In the Michael addition reaction, amines can be added to activated carbon–carbon double bonds under mild conditions.[18]

The catalytic effect of the synthesized PEI-TA in the anionic curing of DGEBA resins has been studied by adding different proportions of this HBP to the formulations by monitoring the curing evolution by DSC. The materials prepared have been characterized by thermogravimetry (TGA), thermomechanical analysis (DMTA) and scanning electron microscopy (SEM) and compared to the conventional DGEBA thermosets obtained by using 1-MI as initiator.

2. Experimental section

2.1 Materials

Hyperbranched poly(ethyleneimine) (PEI) Lupasol G100 (M_w = 5000 g/mol, M_n = 3600 g/mol) was kindly donated by BASF SE (Ludwigshafen, Germany) and used without further purification. From the molecular weight of the polymer and of the

repeating unit an average degree of polymerization of 84 was calculated.[19] The equivalent number of primary, secondary and tertiary amines per mol of PEI is 27.2, 31.4 and 25.4, respectively.[19]

1-Methylimidazole (1-MI), 1-bromopentane, methyl acrylate, sodium azide, propargyl acrylate and CuI from Sigma-Aldrich were used without further purification. Solvents were purchased from Scharlab. Diglycidylether of bisphenol A (DGEBA) Araldite GY 240 was kindly provided by Huntsman (EEW = 182 g/eq).

2.2 Synthesis of propargyl-terminated hyperbranched poly(ethylenimine) (PEI-yne) (Scheme 1)

In a 100 mL two neck round-bottomed flask provided with magnetic stirrer, addition funnel and argon inlet, 1 g of PEI (Lupasol G100, 0.2 mmol, 11.7 meq of reactive amine, NH and NH_2) and 1.29 g of propargyl acrylate (11.7 mmol) were dissolved in a mixture of MeOH/H_2O (50:1 v/v). The reaction mixture was stirred at 40ºC for one day. The solvents were evaporated and the yellow oil was dried under vacuum during two days.

Tg (by DSC) = -41 ºC

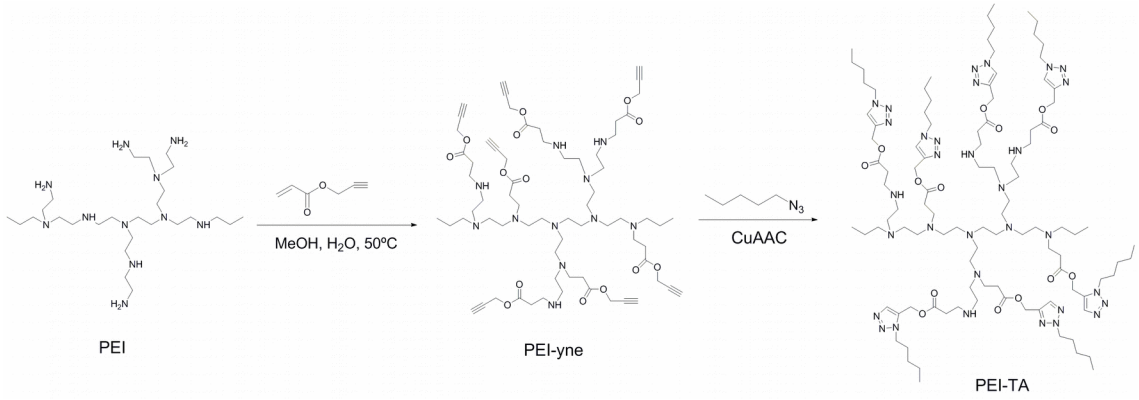
Thermal stability determined by TGA in N_2 atmosphere. $T_{5\%}$= 285 ºC and T_{max}= 378ºC.

Elemental analysis: 50.37 %C, 8.30 %H, 9.60 %N. On basis of this result 92% of modification was calculated, taking into account that both primary and secondary amino groups in PEI react only once.

M_w (g/mol) = 22,100 and M_n (g/mol) = 17,100 both determined by SEC-MALLS in DMAc; M_w/M_n = 1.29; M_w (g/mol) = 10,936 calculated taking into account the modification degree obtained by elemental analysis M_w = M_w PEI + (58.6 x 0.92 x 110.1).

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 3.7 (-COO-C**H**$_2$-C≡C-), 2.8 (-NH-C**H**$_2$-C**H**$_2$-COO-), 2.7-2.4 (broad signal of PEI methylene protons) and 2.45 (**H**-C≡C) (see Figure 1).

^{13}C-NMR (100.6 MHz, DMSO-d_6, δ in ppm): 172.4 (-**C**OO-), 84.1 (-**C**≡CH), 74.7 (-C≡**C**H), 54-50 (broad signal of PEI methylene carbons), 51.1 (-COO-**C**H_2-C≡C-), 48.9 (-NH-**C**H_2-CH_2-COO-) and 32.0 (-NH-CH_2-**C**H_2-COO-).



Scheme 1. Synthetic pathway to the preparation of the multifunctional macroinitiator

2.3 Synthesis of 1-azide pentane

The organic azide was synthesized from the corresponding bromide.[20] In a 100 mL two neck round-bottomed flask provided with magnetic stirrer and argon inlet, 1-bromopentane (5 g, 33 mmol) was dissolved in 40 mL of DMSO. Sodium azide (2.15 g, 33 mmol) was added in one batch and the solution was stirred overnight at room temperature and then water was added slowly. The product was extracted with diethyl ether, which was then washed with brine, dried over sodium sulfate and the solvent removed producing a clear liquid.

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 3.09 (-C**H**$_2$-N_3), 1.46 (-C**H**$_2$-CH_2-N_3), 1.15 (-C**H**$_2$-) and 0.76 (C**H**$_3$-).

^{13}C-NMR (100.6 MHz, $CDCl_3$, δ in ppm): 48.2 (-**C**H_2-N3), 30.0-29.4 (-**C**H_2-), 22.4 (**C**H_3-**C**H_2-) and 14.1 (**C**H_3-).

2.4 Synthesis of triazole hyperbranched poly(ethylenimine) (PEI-TA) (**Scheme 1**)

The click reaction was performed according to a reported procedure.[21] PEI-yne (0.5 g, 0.046 mmol, 2.5 meq) and 1-azide pentane (0.28 g, 2.5 mmol) were dissolved into 10 mL of dry DMF. To the resulting mixture 0.48 g (2.55 mmol) of CuI was added. The mixture was stirred for 24 h under argon atmosphere at room temperature. FT-IR spectroscopy allowed us to confirm that the reaction was completed by the disappearance of the azide stretching peak around 2100 cm^{-1}. Finally, the product was collected after evaporating the solvent as a viscous green liquid (92% of modification, 22% w/w of triazole content).

T_g = -27 ºC (determined by DSC)

Thermal stability determined by TGA in N_2 atmosphere. $T_{5\%}$= 302 ºC; T_{max}= 337 ºC.

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 7.6 (triazole proton), 4.8 (O-C**H**$_2$-triazole) 4.3 (-C**H**$_2$-N triazole), 3.6 (-NH-C**H**$_2$-C**H**$_2$-COO-), 2.7-2.4 (broad signal of PEI methylene protons), 2.0 (-C**H**$_2$-CH$_2$-triazole), 1.2 (-C**H**$_2$-) and 0.9 (C**H**$_3$-).

^{13}C-NMR (100.6 MHz, DMSO-d_6, δ in ppm): 172.2 (-**C**OO-), 147.8 (quaternary C of triazole), 122.2 (tertiary carbon of triazole), 54.7 (-COO-**C**H$_2$-triazole), 54-50 (broad signal of PEI methylene carbons), 51.2 (**C**H$_2$-N triazole), 49.1 (-NH-**C**H$_2$-CH$_2$-COO-), 35.8 (-NH-CH$_2$-**C**H$_2$-COO-), 31.9 and 30.8 (-**C**H$_2$-), 21.5 (**C**H$_3$-**C**H$_2$-) and 13.8 (-**C**H$_3$).

2.5 Preparation of epoxy thermosets.

Mixtures of DGEBA and PEI-TA or 1-MI were prepared by adding the required amount of the initiator to the epoxy resin and gently heating until it was dissolved and the solution became transparent. The compositions of the formulations studied are summarized in **Table 1.**

Table 1. Notation and compositions of the formulation prepared

Sample	**DGEBA** *(g)*	**PEI-TA** *(g)*	**Triazole** *(phr)*[b]	**1-MI** *(g)*	**1-MI** *(phr)*[b]	**Eq$_{epo}$/Eq$_{ini}$**[a]
1-MI-5.6	0.5	-	-	0.027	5.6	7.9
1-MI-11.2	0.5	-	-	0.055	11.2	3.9
PEI-TA-2	0.5	0.045	2	-	-	18.6
PEI-TA-5	0.5	0.11	5	-	-	7.9
PEI-TA-10	0.5	0.23	10	-	-	3.9

a. Ratio between equivalents of epoxy to equivalents of initiator (imidazole or triazole units)
b. Parts of initiator by hundred parts of resin in weight

2.6 Characterization

^{1}H-NMR (400 MHz) and ^{13}C-NMR (100.6 MHz) measurements were carried out in a Varian Gemini 400 spectrometer. $CDCl_3$ and DMSO-d_6 were used as the solvent. For internal calibration TMS was used as standard.

The determination of the molecular weight of the polymers was performed on an Agilent 1200 pump system (US) equipped with a multi-angle light scattering (MALS) detector (Tristar MiniDawn, Wyatt Technology, DE) and refractive index (RI) detector (Knauer, DE) using LiCl(3g/L)-DMAc as an eluent in a PolarGel-M-column (Polymer Laboratories, UK).

Elemental analysis was performed on a vario MICRO CHNSO and Cl Elemental Analysis (ELEMENTAR Analysensysteme GmbH, DE)

FTIR-680PLUS spectrometer from JASCO with a resolution of 4 cm^{-1} in the absorbance mode, equipped with an attenuated total reflection accessory (ATR) with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR from Specac-Teknokroma).

Raman spectroscopy was performed using the RAMAN Imaging Microscope System alpha300R (WITec GmbH, Ulm, Germany) with a laser wavelength of 532 nm. The laser power was 10 mW and the objective used had a magnification of 20x. The integration time was of 0.5 s for one single spectrum with 500 accumulations. All spectra were smoothed by the Savitzky-Golay method.

Calorimetric analyses were carried out on a Mettler DSC-822e thermal analyzer. Samples of approximately 10 mg were placed in aluminum pans under nitrogen atmosphere. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium-lead-zinc standard (temperature calibration).

Non-isothermal curing of prepared mixtures was performed from 30 to 400 ºC at heating rate of 10 ºC/min. Isothermal experiments were done to determine the thermal curing treatment required for preparing the materials in the oven.

The glass transition temperatures (T_{gS}) of the completed cured materials were determined, by means of a second heating scan at 10 ºC/min after the isothermal curing selected, as the temperature of the half-way point of the jump in the heat capacity when the material changed from glassy to the rubbery state under N_2 atmosphere.

Thermogravimetric analyses were carried out in a Mettler TGA-SDTA 851E thermobalance. Samples with an approximate mass of 8 mg were heated from 30 ºC to 800 ºC at 10 ºC/min in N_2 (100 cm^3/min measured in normal conditions).

Dynamic mechanical thermal analyses were carried out with a TA Instruments DMA Q800. The samples were cured isothermally in a mold (5 mm width and 3 mm thick) at 120 ºC for 2 h, 150 ºC for 1 h and 200ºC for 30 min. The samples were carefully polished to ensure constant dimensions in as much as little variations of dimensions lead to erroneous measurements. The samples were analyzed in three-point bending mode with a support span of 10 mm. The viscoelastic properties of the cured materials were

determined by means of a temperature ramp at 3 ºC/min from 35 to 250 ºC and with a frequency of 1 Hz.

The cryofracture area of the specimens was metalized with gold and observed with a scanning electron microscope (SEM) Jeol JSM 6400 with a resolution of 3.5 nm.

3. Results and Discussion

3.1 Synthesis and characterization of PEI-yne

Michael addition reaction has been used to build polymers with different topologies, because of its efficiency and selectivity derived from its *click* nature.[22,23]As detailed in the experimental part, the average number of active amines per molecule (27.2 primary and 31.4 secondary amines) in the PEI structure is globally 58.6. To investigate the degree of modification achievable by Michael addition reaction a first study using 85.8 mol of methyl acrylate per mol of PEI was done, since the hyperbranched character and the different reactivity of primary and secondary amines could reduce the expected modification. Once the reaction was finished, we could prove that the consumption of methyl acrylate was not complete, which was an evidence of the lower global functionality of the PEI molecule. It was reported for Michael addition reactions[24] that secondary amines formed by this process were unable to further react with acrylic compounds and therefore they remain unreacted. Taking this into account, it should be considered that both primary and secondary amines act as monofunctional units and the number of acrylate groups attached by the Michael addition process at the PEI structure can be in average a maximum of 58.6 per molecule.

According to the above results, the synthesis of propargyl terminated PEI (PEI-yne) was carried out using propargyl acrylate as a Michael acceptor and commercially available poly(ethyleneimine) (Lupasol G100) as a Michael donor as it is represented in Scheme 1. The reaction was performed at 50ºC overnight in a mixture MeOH/water to compatibilize both reactants, since it is known that water is an efficient promoter.[25]

The presence of the triple bond in the synthesized PEI-yne was confirmed by Raman spectroscopy (absorption at 2125 cm^{-1}) since the low content of alkyne moieties in the PEI structure did not give an adequate signal in the FTIR spectrum.

The structure of the PEI-yne was determined by ^{1}H and ^{13}C-NMR and Raman spectroscopy. In the ^{1}H-NMR spectrum represented in Figure 1 we can see the presence of the methylene protons (**a** and **b**), appearing as an unresolved signal at ≈ 2.8 ppm in

addition to the propargylic methylene (**c**) and methine (**d**) protons at δ = 3.7 and 2.45 ppm, respectively. Acetylenic proton overlaps with signals of the PEI nucleus. The signals in the ^{13}C-NMR spectrum (detailed in the experimental part) also agree with the ones expected for the modified structure with two significant signals at δ = 84.1 and 74.7 ppm, attributed to the acetylenic carbons.

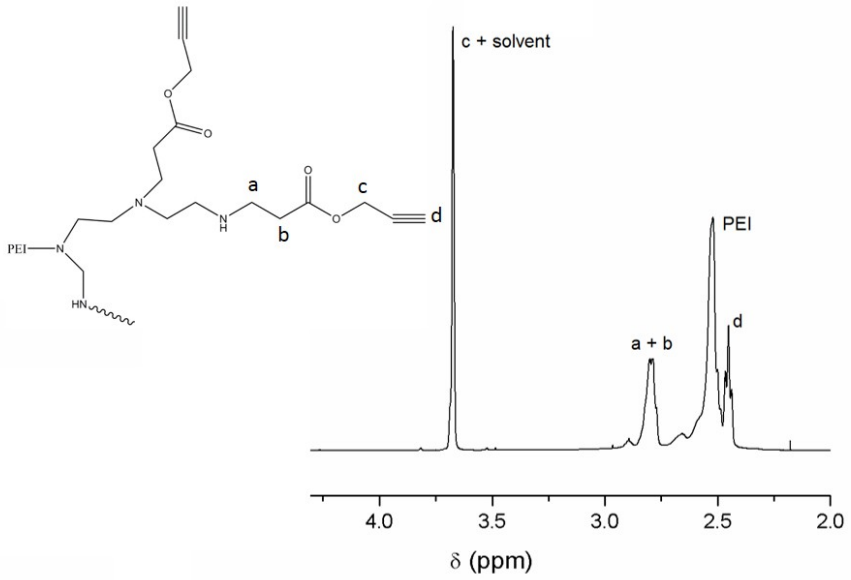


Figure 1. ^{1}H-NMR spectrum of PEI-yne in $CDCl_3$ as the solvent

Although in previous synthetic studies based in PEI structures the degree of modification achieved was calculated by ^{1}H NMR spectroscopy, in the present study it was not accurate enough.Error: Reference source not found,[26] The higher molecular weight of the starting PEI polymer leads to the broadening of the signals together with the overlapping of the nucleus signals with acetylenic protons. This prevents the calculation of the achieved degree of modification. For this reason, the degree of modification of the PEI was calculated by elemental analysis following a reported procedure and resulted to be 92%.[27] The molecular weight of the PEI-yne synthesized was determined by SEC chromatography using a MALLS detector as detailed in the experimental part.

3.2 Synthesis and characterization of PEI-TA

The transformation of acetylenic groups of the previously synthesized PEI-yne to 1,2,3-triazole (PEI-TA) was done by the well-known CuAAC reaction.Error: Reference source not found- It is reported that polar solvents favor the heterocyclic bond formation step and the solubility of the catalyst.Error: Reference source not found In the case of the CuI as the catalyst the formation of a cluster has been reported.[28] In the present case, PEI-yne was reacted with 1-azide pentane in the presence of CuI in solution of DMF at room temperature in an inert atmosphere. After 24 h, the reaction was stopped since by FTIR measurements the total disappearance of the azide stretching peak at 2100 cm^{-1} was observed (Figure 2).Error: Reference source not found[29,30]

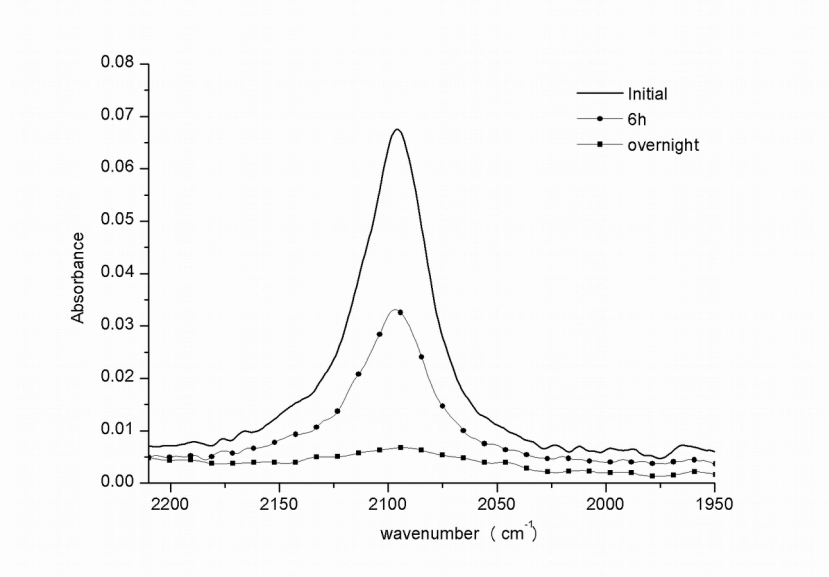


Figure 2. FTIR azide absorptions region taken from the reaction mixture at different reaction times.

Since the acetylene group was not detected by FTIR, Raman spectra of the initial azide, PEI-yne and PEI-TA samples were registered. Figure 3 shows the region of the spectra between 2040 and 2160 cm^{-1} in which the absorption of acetylenic band at 2130 cm^{-1} and of the azide band at 2100 cm^{-1} appear. In the spectrum of PEI-TA both bands are not detected, which confirms that the complete reaction was achieved.

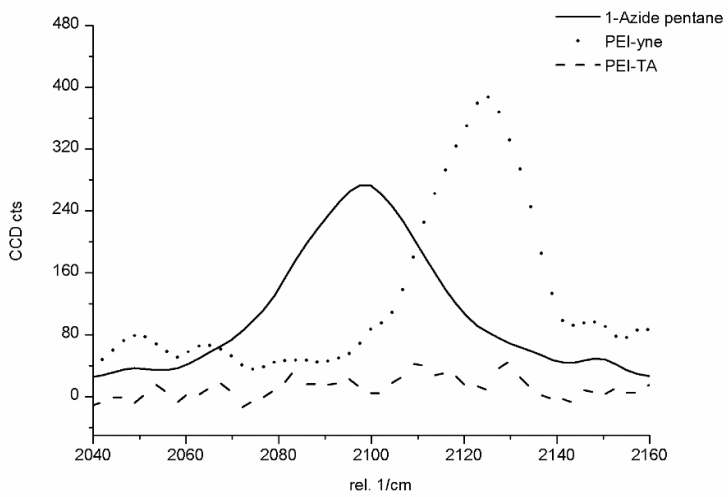


Figure 3. Acetylene and azide absorptions region of the Raman spectra taken for azide, PEI-yne and PEI-TA samples.

The structural characterization of the 1,2,3-triazole containing HBP (PEI-TA) was done by NMR spectroscopy. Figure 4 presents the ^{1}H-NMR spectrum of this polymer. The most significant signal corresponds to the triazole proton (**d**) appearing at 7.6 ppm. In addition, some signals have been shifted significantly in reference to the starting products. Protons in **c** position are shifted from 3.7 in PEI-yne to 4.8 ppm and protons in **e** position, appearing at 3.09 in the 1-azide pentane shift to 4.3 ppm in the spectrum of this polymer. It should be noted the total absence of the most significant signals of the starting material PEI-yne (Figure 1), which accounts for a complete modification by azide-yne click reaction.

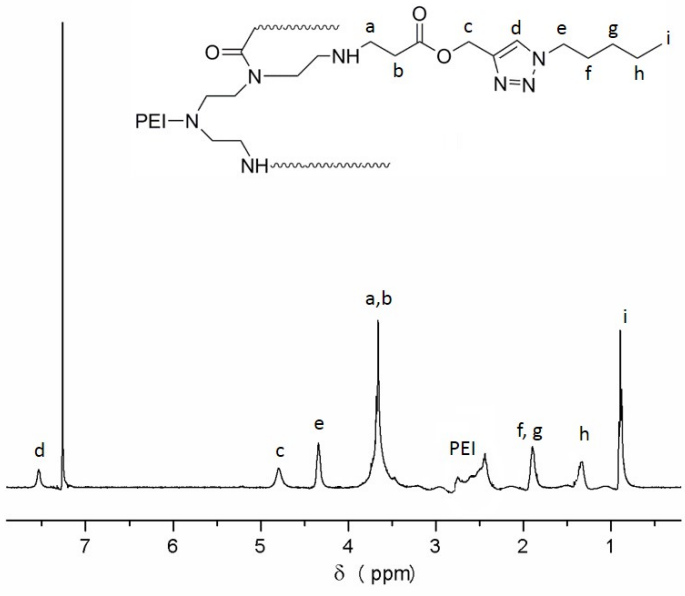


Figure 4. ^{1}H-NMR spectrum of PEI-TA in $CDCl_3$ as the solvent

3.3 Study of the curing process

As reported, the nucleophilic character of imidazoles is able to promote anionic homopolymerization of epoxides.[31] In previous studies, 1-MI was used as initiator and 5 phr were needed to complete the cure of DGEBA formulations.[32,33] According to that, we selected this proportion of triazole groups in DGEBA formulations (Table 1) to investigate the initiating ability of the triazole in the PEI-TA structure. A lower and a higher proportion of PEI-TA were also tested to better understand their effect on the kinetics. Table 1 presents the composition of the formulations studied. Figure 5 shows the non-isothermal DSC curves at 10ºC/min of the formulations containing the different proportions of PEI-TA.

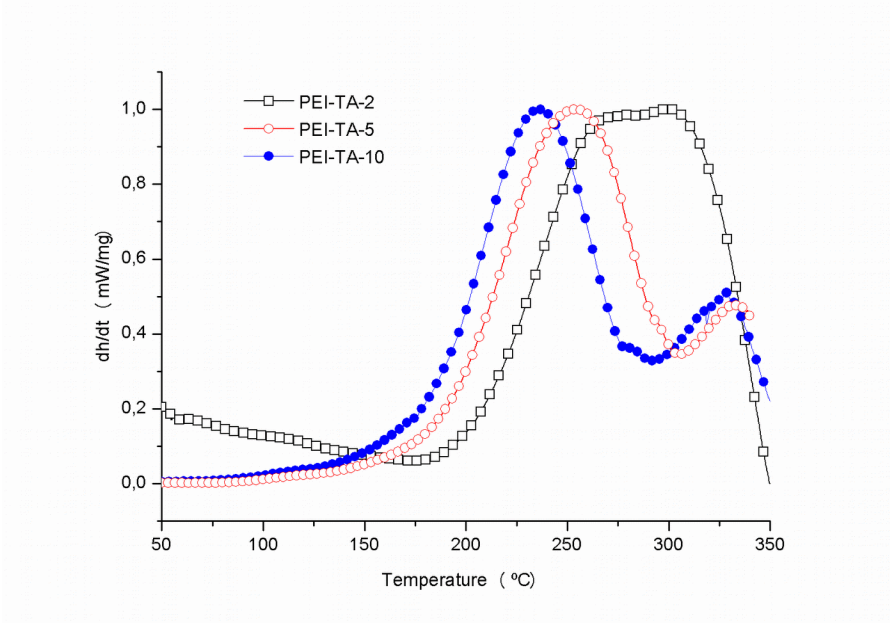


Figure 5. Calorimetric curves registered at 10ºC/min in N_2 atmosphere of the different formulations studied with 2, 5 and 10 phr of triazole groups.

The formulation containing 5 phr of triazole groups (PEI-TA-5) presents the maximum of the peak at 250ºC. In previous papers,Error: Reference source not found,Error: Reference source not found we reported that on using 5 phr of 1-MI the maximum of the peak was at 125ºC. On increasing the proportion of triazole to 10 phr (sample PEI-TA-10) only a slight acceleration was observed and the maximum of the peak is shifted to 220ºC, higher than the temperature at which the curing takes place using 1-MI. The high viscosity of PEI-TA prevents to increase the proportion of this HBP in the reactive mixture and therefore the highest proportion leading to homogeneous mixtures is 10 phr. In a previous study on self-curable epoxy resins with triazole in their

structure,Error: Reference source not found temperatures of the maximum of the exotherm between 200 and 240ºC could be measured. However, in that case 18 phr of triazole groups were present in the reactive formulation. All these results suggest a lower reactivity of triazole, with a lower nucleophilicity than imidazole. This fact can be rationalized on the basis of the lower electronic density of triazole nitrogen than of imidazole. It should also be noticed that in contrast to previously published results,Error: Reference source not found the calorimetric curves are bimodal with a noticeable exotherm above 300ºC (Figure 5). This exotherm could be due to an uncatalyzed thermal homopolymerization of epoxides. The reason could be searched in the topological restrictions to the attack of the nucleophilic species (triazoles) to the oxirane ring. However, a partial degradation of the network structure cannot be discarded, since PEI derivatives are degraded at temperatures about 300ºC.Error: Reference source not found As we can see in Figure 5, reducing the proportion of triazole in the reactive mixture (sample PEI-TA-2) the exotherm at higher temperature is clearly enhanced and the maximum of the first exotherm is shifted to higher temperatures as expected. The growing of the second exotherm on decreasing the proportion of PEI-TA in curing reaction is an indication that thermal homopolymerization of epoxides plays an important role in these curing processes. Taking these results into account, only the samples PEI-TA-5 and 10 were selected to follow up the study.

It should be considered that unreacted secondary amine groups were also present in the PEI-TA structure and they could react with epoxy groups. This reaction was taking place before 150 ºC in a previous study on the reaction of unmodified PEI with DGEBA.[34] From DSC curves it is not clear if this reaction occurs, but in any case it will contribute to the increase in the crosslinking density.

Although it is convenient to determine the enthalpies from the curing exotherms to confirm that a complete conversion of epoxides is achieved, the complex shape of the DSC curves for these formulations prevents an accurate determination of these enthalpies.

Isothermal experiments were carried out to find out the adequate cure schedule to reach materials without any degradation, by looking at the highest T_g value reached. The curing schedule which was selected to prepare the materials for their characterization was the following: 120ºC for 2h, 150ºC for 1h and 200ºC for 30 min.

3.4 Characterization of thermosets

The thermomechanical characteristics of the thermosets were determined by DMTA and compared with those of neat thermosetting polymers prepared by using 1-MI as initiator in comparable proportions as shown in Table 1. Figure 6 shows the variation of tan δ and the storage modulus (E') plots against temperature for all the materials prepared and Table 2 collects the main data extracted from these analyses.

As it can be observed, the shape of the tan δ curves in the temperature range studied is in all cases unimodal indicating homogeneous characteristics of these materials. It can also be seen that the addition the PEI-TA to the formulation in comparison to 1-MI thermosets decreases the temperatures of the maximum of tan δ and the storage modulus in the rubbery region in comparison to 1-MI materials, according to the higher flexibility of PEI structure and to the lower content of rigid DGEBA in PEI-TA formulations.

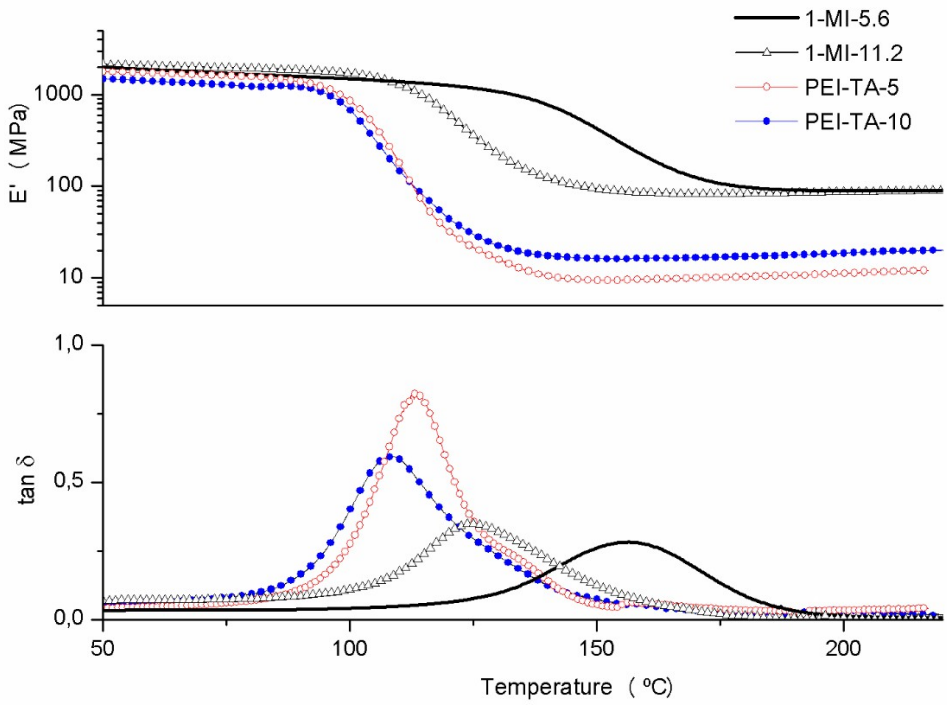


Figure 6. Storage modulus and tan δ evolution against temperature for the materials prepared.

On increasing the proportion of PEI-TA in the formulation the tan δ temperature shifts to lower values, whereas the storage modulus in the rubbery region slightly increases. A similar behavior was observed in thiol-ene/thiol-epoxy materials obtained from allyl terminated hyperbranched PEI.Error: Reference source not found These effects were rationalized on the basis of the higher flexibility of the PEI structure and the lower amount of rigid aromatic moieties coming from DGEBA that leads to a reduction of the transition temperature (tan δ). On the other hand, the small repeating units in the PEI structure lead to a higher number of crosslinking points. Therefore, with increasing the proportion of PEI-TA in the formulation the molecular weight between crosslinks decreases and the storage modulus in the rubbery region increases according to the ideal rubber theory.[35]

It should be noted that the damping characteristics, related to the height of the tan δ curves, are much higher for the novel materials prepared than for standard 1-MI materials in a quite broad range of temperatures, which is valuable from the point of view of toughness enhancement.

Table 2. Thermomechanical and thermogravimetric data for the materials prepared

Formulation	DMTA				TGA	
	$T_{tan\ \delta}$ [a] (˚C)	FWHM [b] (˚C)	Tan δ [c]	E_r [d] (MPa)	$T_{5\%}$ [e] (˚C)	T_{max} [f] (˚C)
1-MI-5.6	157	39	0.26	80	393	437
1-MI-11.3	125	31	0.35	84	378	437
PEI-TA-5	113	18	0.78	8	320	411
PEI-TA-10	108	30	0.59	16	313	408

a. Temperature of maximum of tan δ
b. FWHM stands for full width at half maximum
c. Maximum value of tan δ
d. Storage modulus in the rubbery state determined at tan δ peak + 50ºC
e. Temperature of the onset decomposition on TGA data at 10ºC/min calculated for a 5% weight loss
f. Temperature of the maximum decomposition rate based on the TGA data at 10ºC/min

The thermal stability of the thermosets has been evaluated by thermogravimetric analysis and compared to the materials obtained with 1-MI as initiator. Figure 7 shows the degradation curves and the derivatives obtained and the main data are collected in Table 2.

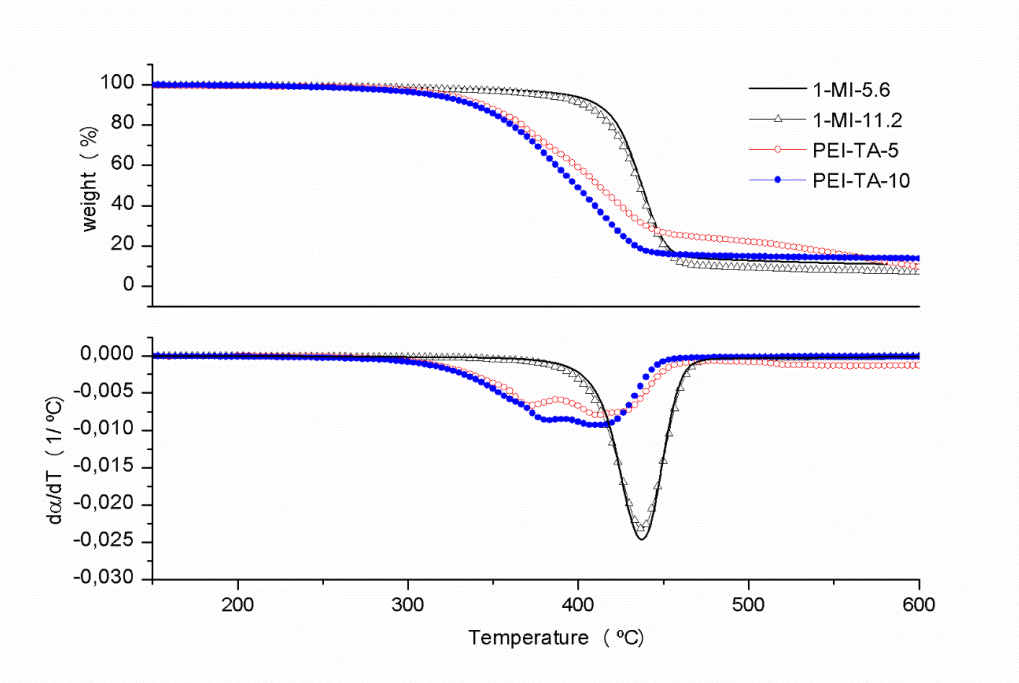


Figure 7. Thermogravimetric curves for the materials prepared.

As we can see, the materials prepared by PEI-TA formulations present a lower stability than 1-MI thermosets and the initial degradation occurs about 70 ºC below than the materials obtained with 1-MI. In addition, the degradative process is much complex, as extracted from the complex shape of the degradation curves. The presence of PEI structure in the materials, with a lower stability than homopolymerized DGEBA is responsible for the decrease in the thermal stability and the prompt degradation of the material.Error: Reference source not found From these thermal studies it can be inferred that curing temperatures should be lower than 300ºC and the curves at high temperature in the non-isothermal DSC scans in PEI-TA-5 and PEI-TA-10 formulations are mainly due to degradation.

The morphology of the materials prepared was examined by SEM from cryofractured samples. The type of fracture is related to the toughness and therefore by examining the fracture surface information about this characteristic can be extracted.

Figure 8 collects the micrographs of the fracture surfaces at different magnifications.

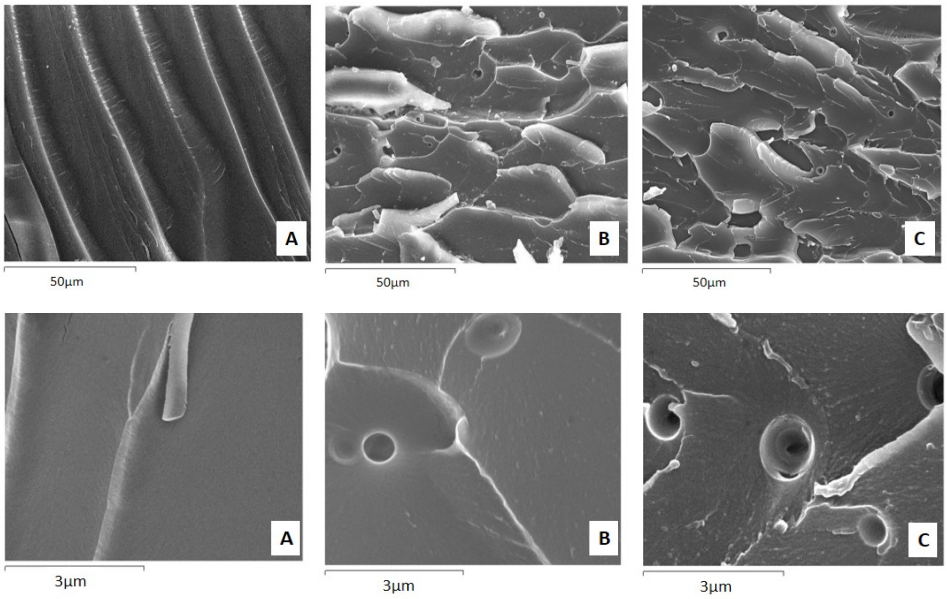


Figure 8. SEM micrographs at 1,000 (up) and 18,000 (down) magnifications of the fracture surfaces of the thermosets obtained from formulations: 1-MI-5.6 (A); PEI-TA-5 (B) and PEI-TA-10 (C)

Whereas the conventional 1-MI initiated material, Figure 8 (A), shows a smooth and fragile fracture with some cracks with little evidence of deformation which accounts for its poor impact resistance, the fracture surfaces of materials containing PEI-TA (Figure 8 B and C up) show a multi-planar nature with tortuous and thicker cracks resulting from plastic deformation and cavitation upon fracture. At higher magnifications (Figure 8 B and C down) it can be appreciated the formation of rubbery particles of submicrometer sizes. These particles help to improve toughness through deviation of cracks and through cavitation mechanisms, increasing the energy absorbed during fracture. The fact that the PEI structure is covalently linked to the DGEBA matrix by the triazole units, acting as initiators, can cause this cavitation effect. In previous studies of our group, phase separation and cavitation have demonstrated good toughness improvements in DGEBA thermosets.Error: Reference source not found The formation of the particles observed could be due to the separation of PEI moieties, which in the present study are derived from PEI with molecular weight of 5,000 D, with a more polar character than homopolymerized DGEBA. In previous studies on the preparation of PEI modified thermosets, the molecular weight of the initial PEI was only 800 D and separation was observed only when PEI modifiers were not covalently linked to the epoxy matrix.Error: Reference source not found[,36]

Conclusions

Michael addition reaction of poly(ethyleneimine) (PEI) to propargyl acrylate was selected to prepare a propargyl modified hyperbranched polymer (PEI-yne), which was reacted with 1-azide pentane following a CuAAC azide-yne click reaction. The structure of the 1,2,3-triazole decorated hyperbranched polymer (PEI-TA) obtained was confirmed by NMR, FTIR and Raman spectroscopy.

PEI-TA was used in different proportions as anionic initiator in the curing of diglycidyl ether of bisphenol A (DGEBA) formulations and calorimetric studies showed a lower reactivity of triazole units in comparison to 1-methylimidazole (1-MI). However, DGEBA/PEI-TA formulations could be cured following an optimized schedule avoiding thermal degradation.

The novel thermosets obtained were thermally characterized and compared to thermosets obtained by using 1-MI as standard anionic initiator. The thermal stability of the novel materials was lower due to the presence of PEI structures that degrades at temperatures about 300ºC. Tan δ and storage modulus are lower than 1-MI materials, but the damping characteristics are better. On increasing the proportion of PEI-TA in the formulation the tan δ decreases due to the flexibility introduced in the network structure by PEI moieties and the reduction of aromatic DGEBA structures.

SEM inspection of the cryofracture surfaces shows the formation of submicron particles in the PEI-TA modified thermosets that leads to a tough fracture with tortuous and thick cracks and presence of cavitation, which should enhance toughness in comparison to the one of the thermosets initiated by 1-MI.

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